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TECHNICAL PAPER proposed for presentation at Thermionic Conversion Specialist Conference sponsored by the Institute of Electrical and Electronics Engineers
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**A SIMPLE EMPIRICAL FORMULATION OF ELECTRON
EMISSION FROM CESIATED METAL SURFACES**

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A SIMPLE EMPIRICAL FORMULATION OF ELECTRON EMISSION FROM CESIATED METAL SURFACES

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Abstract

Cathode emission current densities and anode work functions are necessary inputs to the analysis of thermionic converter systems. These inputs must agree with existing experimental results and be free of ambiguity. A simple empirical equation giving the emission current density in terms of the cesium atom arrival rate and the surface temperature is provided here. The Swanson-Strayer correlation for the maximum change in work function due to cesium adsorption is discussed.

Introduction

Converter analysis would be facilitated by a simple equation giving the electron emission current density J explicitly in terms of the electrode temperature T and the cesium particle arrival rate μ . A need to computer simulate a system containing hundreds of converters makes such an expression even more desirable.

The results must of course agree with existing experimental data. Also the expression must be useable for predictions of J in cases for which there are no experimental data (e.g., for μ larger than in existing data and for untried electrode materials).

Although considerable progress has been made toward a first-principles understanding of the effect of alkali metal adsorption on the electron work function*, there is as yet no basic calculation of J as a function of T and μ . There are a number of semiempirical correlations¹⁻⁹, however, which relate J to T and cesium gas properties (usually the Cs reservoir temperature, T_r). By far the most tested and discussed of these are the classical atomic physics approach of Rasor and Warner⁴ and the molecular chemistry formulation of Levine and Gyftopoulos⁶.

Although both works have in some instances enjoyed agreement with experiment, some basic assumptions of the Rasor-Warner¹⁰⁻¹¹ and Levine-Gyftopoulos¹²⁻¹³ correlations have been brought into serious question. Steiner and Gyftopoulos¹⁴ have refined in part the molecular chemistry approach of Levine and Gyftopoulos. Notable disagreement with experiment has been found for both Levine (or Steiner) - Gyftopoulos and the Rasor-Warner correlations.¹⁵⁻²⁰ While these works at

least can be used as complex data fits, straight forward empiricism can yield a simpler formulation.

We present here a simple and accurate converter surface physics formulation. The result is an explicit equation for J in terms of the bare work function ϕ_0 , μ , and T . Since the derivation is purely empirical, agreement with experiment is improved.

The Cathode

A good deal of information has been obtained empirically about converter cathode surfaces. For example, R. Breitwieser has shown²¹ that his experimental data is such that plots of $\ln J$ versus $\ln P$, where P is the cesium pressure, are nearly linear for a given emitter temperature. Also, it has long been recognized that ϕ versus T/T_r plots (for those experiments for which $\mu = P_{Cs}/\sqrt{2\pi mkT_r}$ and P_{Cs} = vapor pressure of Cs at temperature T_r), are nearly independent of T_r and linear in the range $2.3 \leq \phi \leq 3.3$ eV for the refractory metals, where ϕ is the effective work function*. Some experimenters²² results show a scatter of at most 0.1 eV in ϕ versus T/T_r plots. These workers provide alternate methods of data plotting to reduce data scatter.

Recently, using the "plasma anode" technique²⁰, Houston⁺ has shown that data on the metals W, Pd, Ru, Os, Rh, Ir, and Pt taken at three cesium reservoir temperatures, 414 °K, 434 °K, and 454 °K, "fall on a single curve" when plotted in the form ϕ versus T/T_r . Also his data are nearly linear for $2.3 \leq \phi \leq 3.3$ eV. Thus, it is tempting to write

$$\phi = a T/T_r + b \quad (1)$$

or

$$J = 120 T^2 \exp [-(a T/T_r + b)/kT] \quad (2)$$

where a and b are to be determined empirically. Eqs. (1) and (2) apply only to those cases where $\mu = P_{Cs}/\sqrt{2\pi mkT_r}$. Generalizations will be discussed later.

* $\phi = -kT \ln (J/120T^2)$

+ A preliminary version was presented at the Thermionic Converter Specialist Conference, San Diego, October 25-27, 1965.

* See Ref. 1 for a survey.

If experimental data were available for all candidates for cathode surfaces, then it would be merely necessary to fit for a and b . But of course such data are not available, so it is desirable to also empirically write a and b in terms of cathode properties. The bare work function, ϕ_0 , is a property which distinguishes cathode surfaces, so one might try to find $a(\phi_0)$ and $b(\phi_0)$.

Since the work function of a surface is very sensitive to surface contamination, history of heat treatment, sputtering, bulk impurity content, etc., the following criteria should be satisfied by experiments used to empirically determine $a(\phi_0)$ and $b(\phi_0)$. First, it would be well if all samples were measured in the same tube. Secondly, the bare work functions should be measured when the cesiated data are taken. Fortunately, there are now data available of this nature as taken by two experimenters, Houston²⁰ and Wilson²³⁻²⁴. There is enough disagreement between their results, however, that one needs to make a choice between the two. Houston offers at least plausible arguments for some inaccuracies in Wilson's results, so Houston's data are used here. Such a choice is not necessarily final, however, for as progress is made experimentally, the empirically determined values of a and b can of course be improved.

A least mean square straight line fit was used to determine a and b for the metals reported on by Houston (except for Pd, for which there was insufficient data), and the results are given in Table 1. The r.m.s. deviations of $(a T/T_r + b)$ from the data, Δ_{rms} , and the magnitudes of the maximum deviations, Δ_{max} , are seen to be quite small.

Table 1

Results of l.m.s. Fit for a and b

	$a(\text{eV})$	$b(\text{eV})$	$\Delta_{rms}^*(\text{eV})$	$\Delta_{max}(\text{eV})$	range in ϕ compared (eV)
Pt	1.13	-1.401	0.029	0.044	2.10-3.41
Ir	1.33	-1.87	0.014	0.024	2.04-3.45
Os	1.35	-1.83	0.014	0.033	2.02-3.59
Rh	1.42	-2.09	0.022	0.052	2.31-3.60
Ru	1.43	-1.93	0.031	0.076	2.06-3.55
W	1.48	-1.88	0.013	0.026	2.14-3.26

* Δ = Experimental data point - $(a T/T_r + b)$

As intimated earlier, if one were to stop here, one would be limited to polycrystalline surfaces of the metals studied in Houston's experiment. In searching for a way then to relate a and b to ϕ_0 , one might take note of Houston's plots of T/T_r for a given ϕ versus ϕ_0 . As these plots are nearly linear, one could do a l.m.s. fit to obtain α and β , where

$$T/T_r = \alpha \phi_0 + \beta \quad (3)$$

If this could be done for two values of ϕ , say ϕ_1 and ϕ_2 , then we would have that

$$\begin{aligned} \phi_1 &= a(\alpha_1 \phi_0 + \beta_1) + b \\ \phi_2 &= a(\alpha_2 \phi_0 + \beta_2) + b \end{aligned} \quad (4)$$

and the solutions for a and b as functions of ϕ_0 would follow immediately.

It turns out that rather good fits can be obtained using Eq. (3) for essentially all values of ϕ within the range ~ 2.20 eV to ~ 3.4 eV. Plots of the data including the l.m.s. linear fit for 3.3 and 2.3 eV are shown in figures 1 and 2, respectively. In order to obtain more insight into the limitations of the method, the l.m.s. fit to the Pt group data was extrapolated down to $\phi_0 = 3.5$ eV, for comparison with Houston's²⁰ data on Th and Hf, taken in a separate experiment but using the "plasma-anode" technique. Although we may well not be interested in cathodes with bare work functions of less than say 4.3 eV, it is interesting that at $\phi = 3.3$ eV the extrapolation agrees well with data on both Hf and Th, provided that extensions of the linear portions of the ϕ versus T/T_r curves are used. At 2.3 eV, the agreement is good for Hf but not Th.

If we let $\phi_1 = 3.3$ eV and $\phi_2 = 2.3$ eV, Equations (4) can be solved to yield

$$\begin{aligned} a &= \frac{1}{0.176 \phi_0 - 0.158} \\ b &= 3.3 - a [0.702 \phi_0 + 0.193] \end{aligned} \quad (5)$$

From the preceding, it appears that these results would be useful for $2.3 \leq \phi \leq 3.3$ eV and perhaps for $4.3 \leq \phi_0 \leq 6.0$ eV for Cs on metal substrates.

As a test of the self-consistency of the above procedure, $T/T_r = \alpha_3 \phi_0 + \beta_3$ was fitted at $\phi_3 = 2.0$ eV. Then $a(\alpha_3 \phi_0 + \beta_3) + b$ was compared with 2.8 eV, and found to agree to within ± 0.05 eV for $4.1 \leq \phi_0 \leq 6.5$ eV. Additionally, Table 2 gives the deviations Δ using Eqs. (5). They are larger than in Table 1, but the Δ_{rms} are all less than 0.1 eV.

Table 2

Accuracy Evaluation for Eqs. (5)

	$\Delta_{rms}^*(\text{eV})$	$\Delta_{max}(\text{eV})$	range in ϕ compared (eV)
Pt	0.099	0.17	2.10-3.41
Ir	0.035	0.058	2.04-3.45
Os	0.016	0.028	2.02-3.59
Rh	0.089	0.17	2.31-3.60
Ru	0.054	0.076	2.06-3.55
W	0.021	0.034	2.14-3.26

* Δ = Experimental data point - $(a T/T_r + b)$

But our work is not finished. Eqs. (1) and (2) as written are not useful for converter systems design. First, for a given T , T_r , and cathode surface, ϕ (and hence J) will generally still depend on the converter configuration (interelectrode spacing, wall temperatures, etc.). Second, it would be well if the empiricism could be used in cases where the adsorbate is not coming solely from a vapor, e.g., as in an impregnated cathode where adsorbate is supplied from the substrate.

We can see how Eqs. (1) and (2) could be ambiguous (ϕ depends on more than T and T_r) by using the fact that ϕ and J are unique functions of T and μ for a given cathode surface, where μ is the cesium arrival rate. If, for example, we have an electrode immersed in a gas of temperature T_g , pressure p_g , and particle mass m_g , $\mu = p_g / \sqrt{2\pi m_g k T_g}$. If Knudsen flow conditions apply, $\mu = \mu_0 =$ evaporation rate at the cesium reservoir. But if continuum flow conditions apply, $\mu \approx \sqrt{T_r/T} \mu_0$. So for a given T and T_r , different μ 's and hence different J 's are possible.

Thus to generalize Eqs. (1) and (2) (and thus generalize the usefulness of our already found a 's and b 's), we need to write $T_r = T_r(\mu)$ for the case of Houston's experiment. In Houston's experiment, $P_{Cs} = p_g$ and $T_g = T_r$. Approximating Heime1's²⁵ empirical expression for P_{Cs} , which makes use of recent vapor pressure data, we have*

$$\mu \approx C \exp(-9027/T_r)$$

so that

$$1/T_r = -(1/9027) \ln(\mu/C) \quad (6)$$

$$\text{where } C = 1.193 \times 10^{30} \bar{T}_r^{-1.02},$$

\bar{T}_r = the mean T_r in the range of interest,

the units of μ are particles $\text{cm}^{-2}\text{sec}^{-1}$, and T and T_r are in $^\circ\text{K}$. Values of C for use in converter design are given in Table 3, together with the maximum error in μ caused by the use of \bar{T}_r rather than T_r in C .

Table 3

Arrival Rate Parameter C

$\mu(\text{cm}^{-2}\text{sec}^{-1})$	$C(\text{cm}^{-2}\text{sec}^{-1})$	Max. Disagreement with Heime1's μ
$3.4 \times 10^{17} - 1.1 \times 10^{19}$	2.437×10^{27}	8.9%
$1.1 \times 10^{19} - 1.4 \times 10^{20}$	2.067×10^{27}	7.6%
$1.4 \times 10^{20} - 8.8 \times 10^{20}$	1.794×10^{27}	6.6%

Combining Eqs. (1), (2), and (6), we have

$$\phi = -(aT/9027) \ln(\mu/C) + b \quad (7)$$

* Other adequate vapor pressure relations are available (see, e.g. Ref. 26)

and

$$J = 120 T^2 (\mu/C)^{1.2856} \exp(-11605 b/T) \quad (8)$$

Eqs. (7) and (8), used in conjunction with Eqs. (5) and/or Table 1 will be useful regardless of whether the cesium arrives from a gas under say Knudsen or continuum flow conditions or even if it arrives from the substrate of an impregnated cathode.

The Anode

The temperature requirements on the anode ($< 1200^\circ\text{K}$) are much less stringent than on the cathode. This, of course, gives us much more latitude.

The anode generally has much more surface impurities than the cathode, so Houston's results are not necessarily pertinent to real converter anodes. Still it would improve our understanding of real converter anodes if one could predict the minimum work function of "clean" cesiated anodes.

Although the minimum work function, ϕ_{\min} , is 1.5 ± 0.1 eV for many substrates,^{15,20} it is desirable to have a means of predicting ϕ_{\min} generally, since we have some freedom in choosing anode materials. Swanson,¹⁵ et al. have empirically determined that

$$\Delta\phi_m = 1.09 (1.78 - \phi_0) \text{ (eV)} \quad (9)$$

or

$$\phi_0 + \Delta\phi_m = \phi_m = 1.94 - 0.09 \phi_0 \quad (10)$$

where ϕ_m is the minimum electron work function. Eq. (9) was determined by correlating field-emission data for Cs on Mo, W (Poly), W(100), W(110), Re, Ta, and Ni. Although thermionic measurements are done at much lower fields and higher temperatures, Table 4 shows that Houston's results are in good agreement with Eq. (9). Thus it appears that we may be able to use Eq. (10) for thermionic work functions also.

Table 4

A Test of Eq. (9) Under Thermionic Conditions

	ϕ_0 (eV)	$(\phi_0 - \phi_{\min})$ (eV)	$1.09(\phi_0 - 1.78)$ (eV)
Pt	5.50	3.9	4.05
Ir	5.31	3.7	3.85
Rh	5.25	> 3.7	3.78
Os	5.16	3.7	3.68
Ru	4.89	> 3.3	3.39
W	4.69	> 3.1	3.17
Hf	3.97	> 2.3	2.39

* Ref. 20

Discussion

It would be well to compare the accuracy of our scheme with that of the Levine (or Steiner)-Gyftopoulos and Rasor-Warner correlations using Houston's data. The Steiner-Levine-Gyftopoulos (S.L.G.) schemes require knowledge of not only the bare work function, but also the monolayer work function and cesium coverage. As Houston did not measure these last two quantities, the S.L.G. correlations unfortunately cannot be compared unambiguously. Houston²⁰ compared the calculated (Levine-Gyftopoulos) S-curve properties listed in Table 1 of Ref. 6 with his data (Table 1 was made up assuming a monolayer work function of 1.81 eV and a monolayer coverage of 4.8×10^{14} cm⁻² for Cs on 21 metals). He concluded that "little correlation exists between the experimental results and the theoretical prediction." The predictions of the Rasor-Warner correlation are plotted on Figs. 1 and 2. There we see that at 3.3 eV, the Rasor-Warner predictions agree well with the data. At 2.3 eV, however, the Rasor-Warner correlation is in general disagreement with the data.

Now let us see how our Eqs. (5) and (7) are used in the case of a convertor configuration. Refeh et al.²⁷ have reported on a variable spacing convertor using a (110) oriented vapor deposited tungsten emitter. They found the bare work function of the emitter to be 4.78 eV. The interelectrode spacing of 1 mil was such that at their highest cesium pressure Knudsen flow conditions existed. Using $C = 2.067 \times 10^{-7}$ cm⁻²sec⁻¹ (see Table 3) ($\ln 1/C = -62.90$), and $\phi_0 = 4.78$ eV, we can determine $\phi(\mu)$ from Eqs. (5) and (7). The result is shown to be in quite good agreement with the data in Fig. 3.

It should be made explicit that the relations derived here do not include the effects of strong external fields. In taking this into account (as one might have to in ignited mode operation), it would be well to note Langmuir and Taylor's² finding that the effect of external field on electron emission from cesium coated tungsten is in general larger than for pure tungsten and varies with coverage.

Finally, in order to illustrate the use of the above equations, the zero-field electron emission characteristics are calculated for a convertor with the following properties:

bare work function of the emitter, $\phi_0 = 4.9$ eV

bare work function of the collector,

$\phi_{0c} = 5.0$ eV

emitter temperature, $T = 1900$ °K

collector temperature, $T_c = 850$ °K

$\mu = 1.43 \times 10^{20}$ cm⁻²sec⁻¹ at the emitter

From Eqs. (5), $a = 1.42$ eV and $b = -1.87$ eV. Then from Eqs. (7) and (8) we have (using $C = 1.794 \times 10^{-7}$ cm⁻²sec⁻¹):

$\phi = 3.02$ eV and $J = 4.35$ amp cm⁻²,

where ϕ and J are of course the cathode effective work function and electron emission current density respectively.

If we have a "clean" collector surface, Eq. (10) gives its minimum work function as $\phi_{\min.} = 1.49$ eV.

Summary

An empirical convertor surface physics formulation has been provided which is quite simple and yet agrees better with experiment than other correlations in general use.

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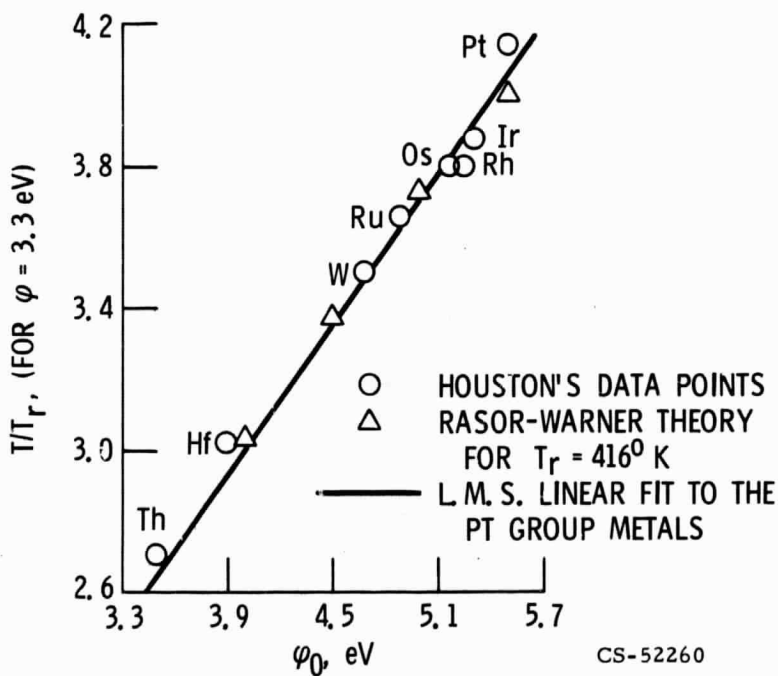


Figure 1. - T/T_r versus substrate bare work function, ϕ_0 , for $\phi = 3.3$ eV.

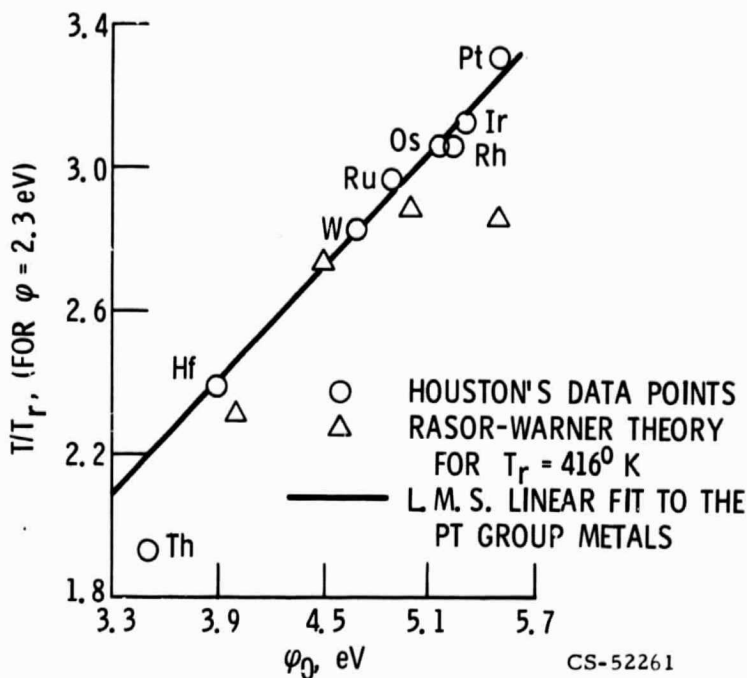


Figure 2. - T/T_r versus substrate bare work function, ϕ_0 , for $\phi = 2.3$ eV.

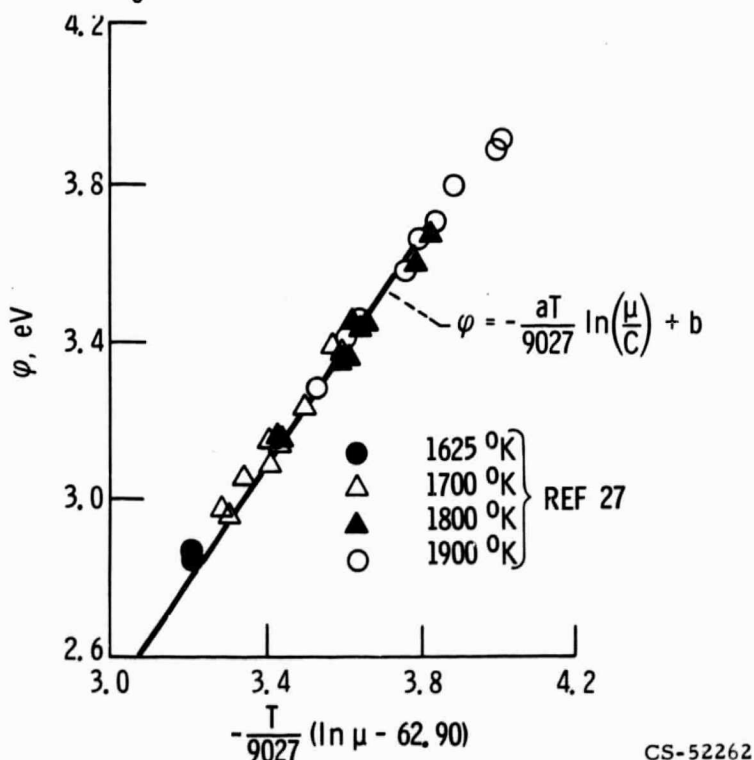


Figure 3. - A comparison of the results of ref. 27 with the predictions of eq. 7, using $\phi_0 = 4.78$ eV.